

# Study of NO adsorption on activated carbons

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## Abstract

Activated carbons (ACs) with varied porous textures and surface chemistry were studied for NO removal under different test conditions at temperatures below 100 °C. When oxygen is absent, there is almost no NO removal. When oxygen is present ACs act both as a catalyst for NO oxidation and as an adsorbent for NO adsorption. NO conversion is correlated with the presence of narrow micropores and is independent of surface area. ACs with an average micropore size around 7 Å exhibit the best NO removal capacity. NO rather than NO<sub>2</sub> was observed to be the main adsorbed species during the initial period of adsorption. NO<sub>2</sub> adsorption and NO<sub>2</sub> gas release start only after the carbon surface was rapidly oxidized during the early stage of adsorption. The decomposition of NO<sub>2</sub> formed through NO oxidation was believed to be responsible for the rapid carbon surface oxidation and NO chemisorption.

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## 1. Introduction

Activated carbons (ACs) have been studied extensively as adsorbents and catalysts for the reduction of NO emission from combustion systems. Laboratory and pilot scale tests [1–4] have demonstrated that NO can be efficiently removed from combustion fuel gas by ACs at temperatures below 150 °C. However, the detailed process of NO removal and the factors which control this process are still a topic of discussion. Kaneko [5] proposed that NO adsorption on activated carbon is a micropore filling process with NO as the adsorbed species. Teng and Suuberg [6] suggested that NO adsorption involves the dimers of NO which convert to N<sub>2</sub> and surface oxides. Other groups [1,7–9] believe that NO was oxidized to NO<sub>2</sub> on the carbon surface and that NO<sub>2</sub> was the adsorbed species. The presence of O<sub>2</sub> was found to be important for NO adsorption in many of the studies [3,4,7–12]. However, it is not clear how the oxygen participates in this process, whether in form of surface oxygen groups, molecularly adsorbed oxygen, or dissociatively chemisorbed oxygen (that is oxygen chemisorbed on carbon surface in a dissociative state but has not reacted with carbon yet). Furthermore, the dependence of NO adsorption on the

carbon type, surface chemistry, surface area and pore volume is not well understood yet.

The main objective of this work is to study the controlling factors in NO adsorption on activated carbons at low temperatures and to gain understanding of the adsorption process. We will examine the influence of carbon texture, surface chemistry, gas concentration, pressure and temperature on NO removal efficiency. We also try to elucidate the NO adsorption mechanism by analyzing the evolution of adsorbed species on carbon at different adsorption stages. We proposed based on experimental observations that NO adsorption takes place mostly at the early stage of adsorption till the carbon surface is oxidized. The main adsorption processes involves: (a) NO reacts with O<sub>2</sub> in narrow micropores to form NO<sub>2</sub>; (b) reaction of NO<sub>2</sub> with un-oxidized carbon surface leads to NO chemisorption and rapid oxidation of carbon surface.

## 2. Experimental

### 2.1. Sample preparation

The samples used were prepared from commercially available SKC carbon molecular sieves (Anasorb<sup>®</sup>, CMS produced by SKC Inc., PA). The as-received carbon sieves (SKC-AR) have a bulk density of 0.56 g/cm<sup>3</sup>, a BET surface area of 977 m<sup>2</sup>/g, and an average micropore size of ~5 Å. Since

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the carbon sieves were made from polymer-based material with an ash content of 0.3%, the influence of mineral content on NO adsorption was believed to be minimal. The as-received carbons were further activated with CO<sub>2</sub> to different degrees of burn-off in a tube furnace (Thermolyne 21101). The activation process includes: (a) heating from ambient temperature to 950 °C under a nitrogen flow with a heating rate of 40 °C/min; (b) holding at 950 °C under a flow of 30 vol.% CO<sub>2</sub> in N<sub>2</sub> for a period of 45–360 min; (c) cooling down to ambient temperature under a nitrogen flow. The flow rate was 1 L/min throughout the process. The burn-offs, surface areas and micropore sizes of the carbons after different activation times are listed in Table 1. In addition, samples of a commercial coconut shell-based activated carbon (PICA) and a high-surface area carbon Maxsorb MSC-30 (Kansai) were also tested for comparison.

## 2.2. Surface characterization

The porous texture of the samples was determined by nitrogen-adsorption isotherms at 77 K using a Micromeritics ASAP 2010 apparatus. The range of relative pressure in the measurement is from 10<sup>−6</sup> to 1. The isotherms were used to calculate the specific area (*S*<sub>DFT</sub>), micropore volume (*V*<sub>mic</sub>), incremental micropore volume, micropore size, and pore size distribution according to density functional theory (DFT) using the data reduction software provided with the instrument. The average micropore size *L*<sub>mic</sub> given in Table 1 was the average width of all the micropores in the range 4–20 Å.

## 2.3. Adsorption and desorption

NO adsorption and temperature-programmed-desorption (TPD) tests were carried out in a quartz flow tube reactor with an inner diameter of 9 mm. A sample of 200 mg carbon was packed into the reactor and a K-type thermocouple was inserted next to the carbon to monitor the sample temperature. The NO gas mixture for adsorption was diluted from gas tanks of 5000 ppm NO/Ar and 21% O<sub>2</sub>/Ar with argon to the desired concentration of 500 ppm NO and 0–10% O<sub>2</sub> through mass flow controllers. The effluent gas from the bypass line or from the reactor was analyzed by an NGA2000 MLT multi-gas analyzer (Fisher, Rosemount, CA) which simultaneously monitors the concentrations of NO, NO<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub>, CO, CO<sub>2</sub>, and O<sub>2</sub> at ppm levels. A quadrupole mass spectrometer (MS) was also attached to monitor the presence of other gases and water.

For NO adsorption, the carbon bed was first purged with Ar at a flow rate of 0.5 L/min for 20 min at ambient temperature. The NO gas mixture at a flow rate of 0.5 L/min was adjusted and stabilized in the bypass line to the desired NO and O<sub>2</sub> concentrations and then switched to the carbon bed in the reactor for adsorption. At a flow rate of 0.5 L/min at 500 ppm NO, the delivery of NO to the system was 0.010 mmol/min. After adsorption for a specific time, the flow of NO gas mixture was stopped and the carbon bed was purged with Ar (0.5 L/min) until the NO and NO<sub>2</sub> concentrations in the effluent gas decreased to less than 15 ppm. After argon purge, a TPD test was run immediately in Ar (0.25–0.5 L/min) at 10–20 °C/min up to 200 °C (NO-TPD) or 950 °C (O-TPD) to examine species emitted from the carbon. The NO-TPD was run to 200 °C because we found that most of the adsorbed NO and NO<sub>2</sub> were desorbed at temperatures below 200 °C in this study. The O-TPD was run to 950 °C for some carbons to evaluate the presence of surface oxygen groups on carbons by monitoring the evolution of CO and CO<sub>2</sub> during TPD. NO conversion was calculated from the inlet NO concentration (*C*<sub>in</sub>) and outlet NO concentration (*C*<sub>out</sub>) as conversion = (*C*<sub>in</sub> − *C*<sub>out</sub>)/*C*<sub>in</sub> × 100%.

Step-response experiments were carried out to study the effect of pressure, temperature, and concentrations of NO and O<sub>2</sub> on NO conversion. For these experiments, a NO gas mixture was fed into the carbon bed for at least 2.5 h to allow steady-state NO conversion being approached. Then one of the test parameters was changed until NO concentration reached a new steady state. To test the pressure effect, a needle valve was installed next to the reactor outlet in order to control the pressure in the reactor. The pressure in the reactor was measured by the pressure gauges.

## 3. Results

### 3.1. Effect of carbon texture on NO conversion

Fig. 1 shows the nitrogen-adsorption isotherms of several ACs being used in this study. The SKC-AR has a very closed knee due to its homogeneous distribution of narrow micropores (~5 Å). The micropores widen with burn-off, and the SKC-360 has mostly of micropores above 9 Å. The texture properties of these carbons are summarized in Table 1.

Fig. 2 shows the break-through curves for NO adsorption on SKC carbons with different degrees of activation. In the presence of 10% O<sub>2</sub>, the outlet NO concentration is always

Table 1  
Textural properties and NO conversions of activated carbons used in this study

Carbon	Activation time (min)	Burn-off (%)	<i>S</i> <sub>DFT</sub> (m <sup>2</sup> /g)	<i>V</i> <sub>mic</sub> (cm <sup>3</sup> /g)	<i>V</i> (5–8 Å) (cm <sup>3</sup> /g)	<i>V</i> (9–15 Å) (cm <sup>3</sup> /g)	<i>L</i> <sub>mic</sub> (Å)	NO (%)
SKC-AR	0	0	1357	0.39	0.12	0.04	5.7	22
SKC-45	45	12	1342	0.41	0.14	0.07	6.6	46
SKC-90	90	19	1612	0.54	0.23	0.14	7.2	52
SKC-180	180	33	1804	0.72	0.18	0.27	9.3	44
SKC-360	360	52	1901	0.91	0.17	0.37	12.2	36
PICA	–	–	1045	0.46	0.12	0.17	11.1	31
MSC-30	–	–	1553	0.58	0.14	0.24	12.3	31

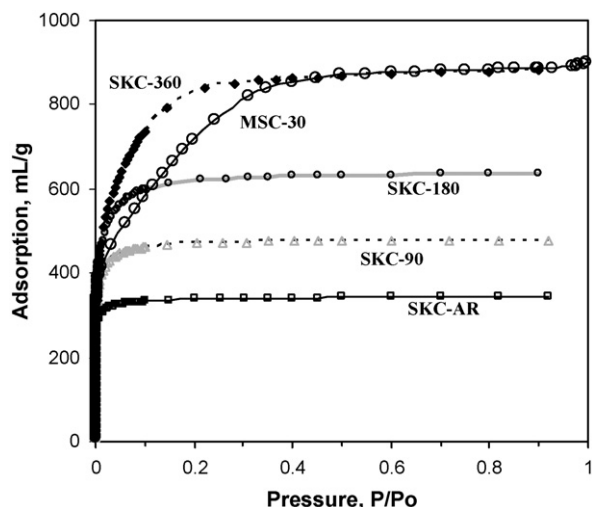


Fig. 1. Nitrogen-adsorption isotherms (77 K) for some of the carbon samples studied.

lower than the inlet concentration of 500 ppm for all the tested carbons. Emission of  $\text{NO}_2$  was detected after adsorption for 5–10 min, and its concentration then rose slowly with time to a steady state. The observation of  $\text{NO}_2$  emission suggests strongly that some of the NO was oxidized to  $\text{NO}_2$  over-activated carbon in the presence of oxygen, in agreement with previous reports [1,4,7–11]. As can be seen in Fig. 2, NO outlet concentration is the highest on SKC-AR, and it is lowest on SKC-90, although the SKC-360 has the largest surface area. The NO conversion has a strong dependence on the average micropore size (Fig. 3a) but has no direct relationship with surface area (Fig. 3b). A maximum conversion was observed on carbon with the average micropore width around 7 Å (SKC-90). This conclusion appears to be general for other carbons too, because the data of PICA and Maxsorb (MSC30) carbons fall on the same trend (Fig. 3a). Note in Table 1 that the NO conversion appears to have a good correlation with the micropore volume of 5–8 Å pores but bear no relationship with the micropore volume of 9–15 Å pores. The NO conversion on SKC-360 with a large volume of 9–15 Å pores is lower than that of the SKC-90 with mostly 5–8 Å micropores.

The NO to  $\text{NO}_2$  conversion on ACs is sustainable as demonstrated in a relatively long-term adsorption test on SKC-45 carbon for 24 h. It was observed that  $\text{NO}_2$  concentration reached its peak value at about 2.5 h while NO release was close to a steady state. After 6 h, the sum of NO and  $\text{NO}_2$  was balanced to the inlet NO concentration, meaning that all the consumed NO was converted into  $\text{NO}_2$ . The result indicates that ACs act as a catalyst for NO oxidation at room temperature.

### 3.2. Effect of surface oxygen groups on NO conversion

Since the surface oxygen groups on carbon may play a certain role in NO adsorption, thermo-desorption tests were run to 950 °C on several SKC carbons. During desorption, the surface oxygen containing groups will decompose as  $\text{CO}_2$

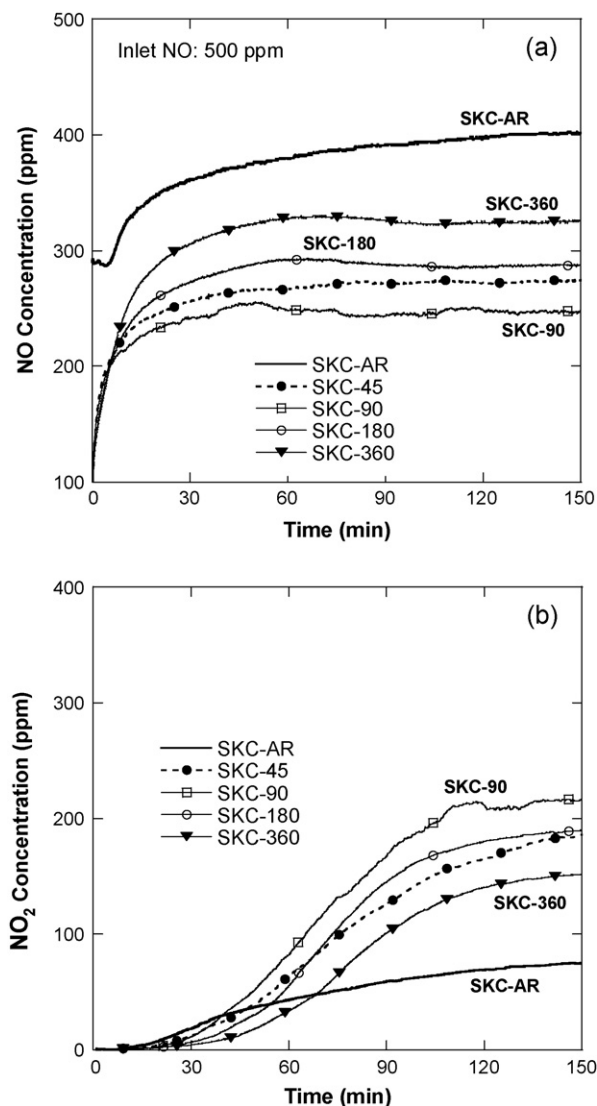


Fig. 2. The effluent (a) NO and (b)  $\text{NO}_2$  concentrations during adsorption in the mixture of NO and  $\text{O}_2$  at 25 °C on SKC carbons after different degrees of activation. Inlet gas: NO, 500 ppm;  $\text{O}_2$ : 10%; Ar, balance; total flow rate, 0.5 L/min; AC: 0.2 g.

(from carboxyl, lactonic groups and their derivatives) and CO (from quinones, hydroquinones and phenols) [13,14]. The CO and  $\text{CO}_2$  evolution profiles for SKC-AR, SKC-45, and SKC-360 are shown in Fig. 4. The as-received SKC carbon exhibits the highest CO and  $\text{CO}_2$  release while the SKC-360 has the lowest (Table 2). The amount of surface oxygen groups on SKC carbons appears to decrease with the activation time. Considering the NO conversion behavior shown in Fig. 2, we may conclude that there appears to be no direct relationship between NO conversion and the amount of surface oxygen groups in the studied experimental conditions. However, the surface oxygen groups appear to affect the starting point of  $\text{NO}_2$  release during adsorption. The SKC-AR with the highest amount of surface oxygen groups shows the earliest release of  $\text{NO}_2$  even though its NO conversion is the lowest (Fig. 2b). The SKC-360 with the least amount of surface oxygen groups is the latest in  $\text{NO}_2$  release.

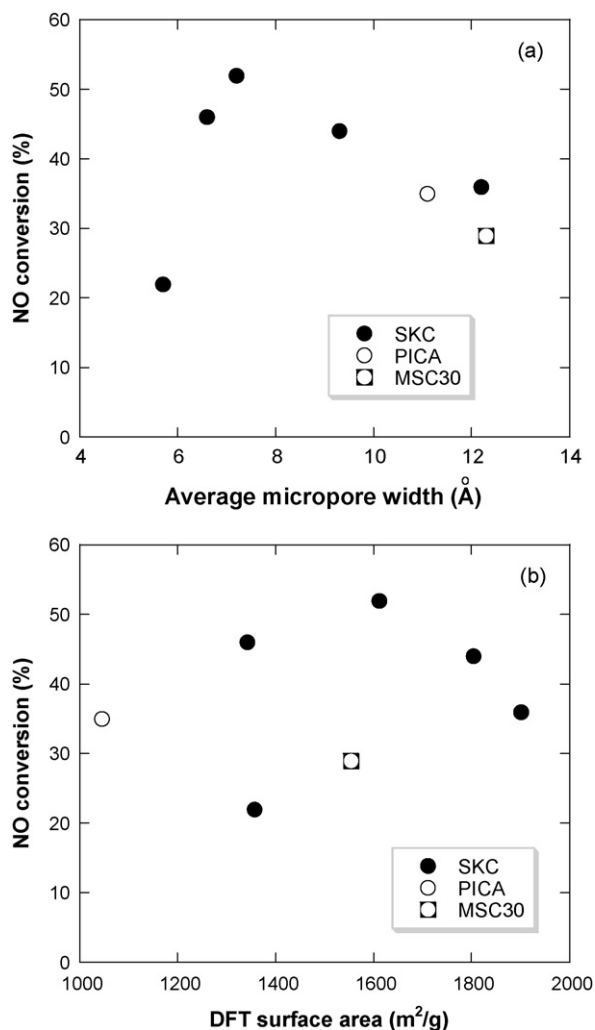


Fig. 3. The dependence of NO conversion on (a) micropore size and (b) surface area of various ACs after adsorption for 2.5 h at 25 °C. Inlet gas: NO, 500 ppm; O<sub>2</sub>: 10%; Ar, balance; total flow rate, 0.5 L/min; AC: 0.2 g.

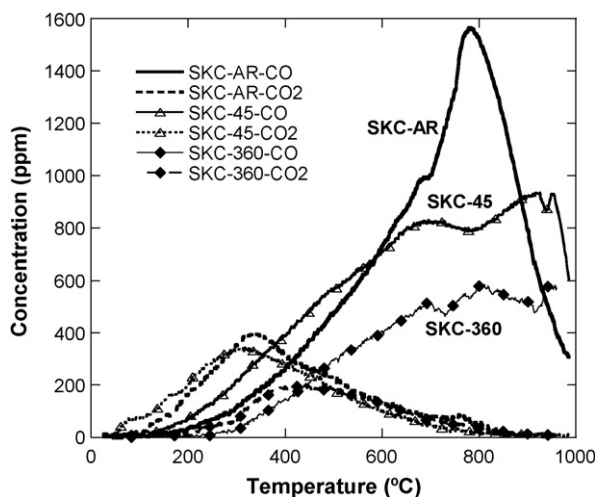


Fig. 4. Evolution profiles of CO and CO<sub>2</sub> during TPD for SKC carbons without NO adsorption. Heating rate: 20 °C/min; Ar: 0.25 L/min; AC: 0.2 g.

Table 2

Amounts of CO and CO<sub>2</sub> desorbed during TPD to 950 °C from SKC carbons (mmol/g)

Carbon	CO	CO <sub>2</sub>	Total
SKC-AR	1.49	0.37	1.86
SKC-45	1.34	0.33	1.67
SKC-360	0.93	0.2	1.13

### 3.3. Effect of test conditions on NO conversion

NO conversion on SKC carbons depends strongly on temperature and gas pressure. The steady-state NO conversion was observed to increase when increasing pressure or decreasing temperature. At 100 °C, NO conversion is less than 5%. The dependence of NO conversion on oxygen and NO concentrations is shown in Fig. 5. NO conversion increases with NO concentration up to 500 ppm and then becomes independent above this level. Meanwhile, NO conversion depends strongly on oxygen concentration (Fig. 5b). This reaction most likely involves the dissociation of molecular oxygen because NO conversion, and correspondingly, the reaction rate are proportional to the square root of oxygen concentration. As can be seen, the dependence of reaction rate on NO concentration and temperature was calculated and shown in Fig. 6. The order

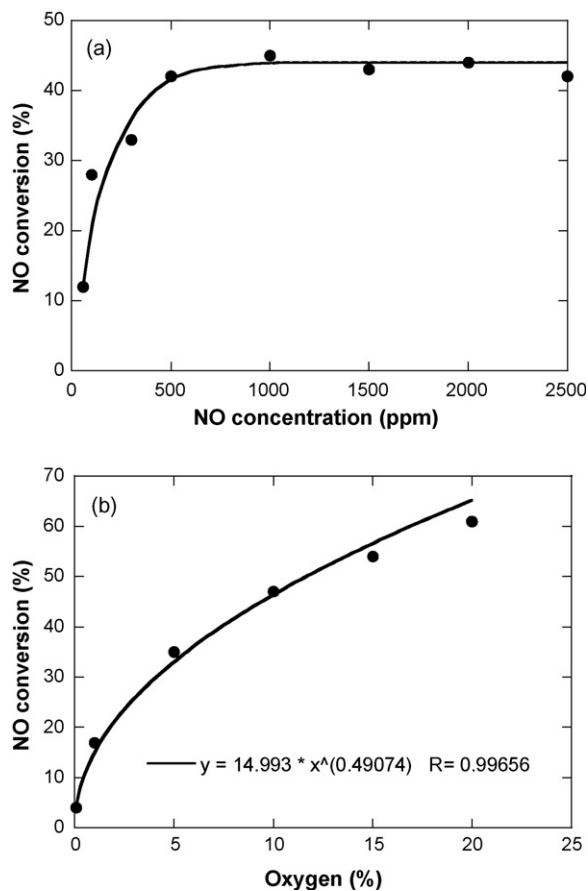


Fig. 5. The dependence of steady-state NO conversion on (a) NO concentration at 10% O<sub>2</sub> and (b) O<sub>2</sub> concentration at 500 ppm NO in feed gas at 25 °C on SKC-45 carbon.

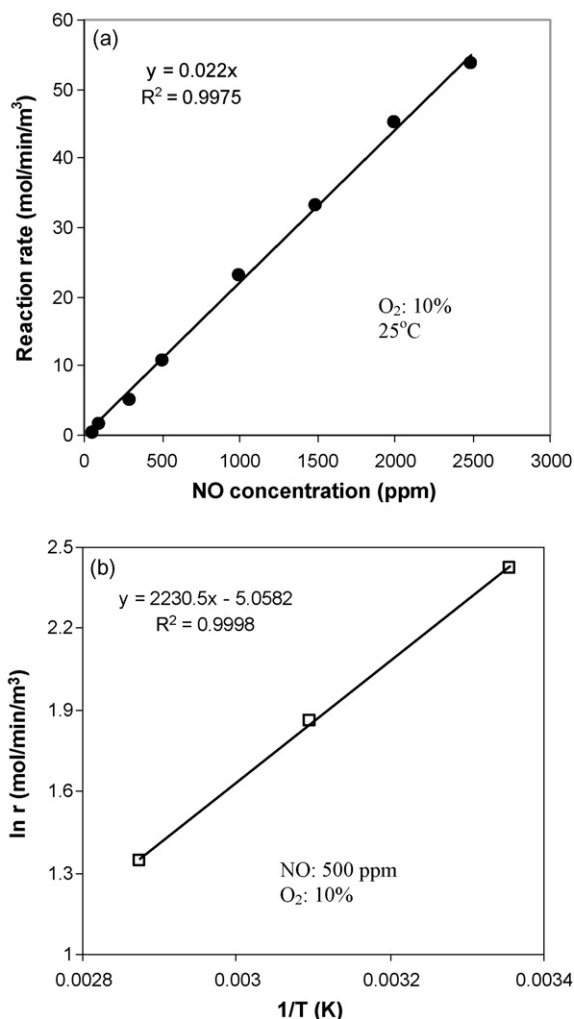


Fig. 6. The dependence of reaction rate ( $r$ ) on (a) NO concentration at 10% O<sub>2</sub> and on (b) temperature on SKC-45 carbon.

of reaction with respect to NO is close to unity. The apparent activation energy for this reaction was calculated from Fig. 6b to be  $-18.5$  kJ/mol.

### 3.4. Temperature-programmed-desorption (TPD)

To examine the species adsorbed on carbon during the NO adsorption process, TPD tests were run for SKC-45 samples after adsorption for 5 min, 30 min, 1 h, 2.5 h, and 24 h in a gas mixture of 500 ppm NO and 10% O<sub>2</sub>. Fig. 7 presents the desorption spectra of samples after adsorption for 5 min and 2.5 h. Note first that the major desorbed species after adsorption for 5 min are NO, O<sub>2</sub>, and CO<sub>2</sub> (Fig. 7(a)). The amount of desorbed NO<sub>2</sub> is marginal. But after adsorption for 2.5 h, a substantial amount of NO<sub>2</sub> was observed. The second important point to be noted is the concurrent desorption of O<sub>2</sub>, CO<sub>2</sub>, and CO. These desorption peaks were not observed in the blank samples without NO adsorption. Note also that the peak temperatures for CO and CO<sub>2</sub> desorption are below 150 °C. There were no additional peaks of NO and NO<sub>2</sub> being observed above 200 °C. The distribution of NO and NO<sub>2</sub> spectra in the

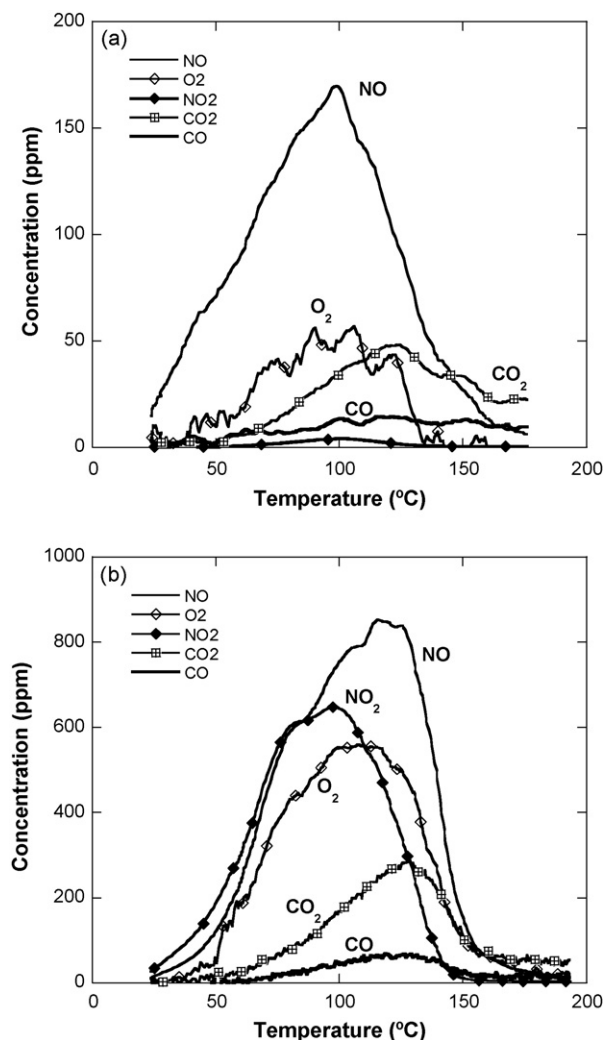


Fig. 7. Desorption spectra of SKC-45 carbons after NO adsorption at 25 °C for (a) 5 min and (b) 2.5 h in a gas flow of 500 ppm NO and 10% O<sub>2</sub>. TPD: 10 °C/min; Ar flow: 0.5 L/min.

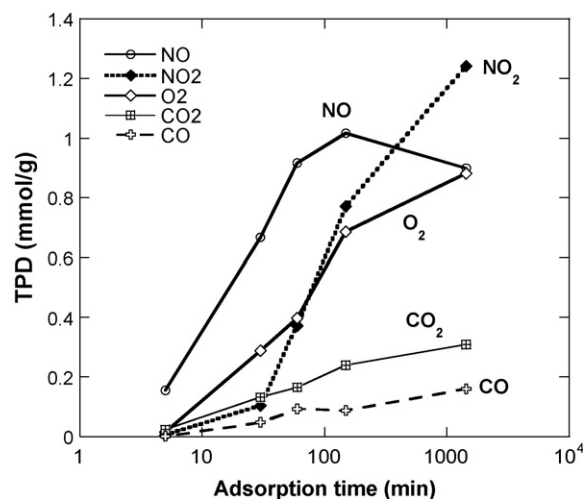


Fig. 8. Variation of the total amount of desorbed NO, NO<sub>2</sub>, O<sub>2</sub>, CO and CO<sub>2</sub> during TPD as a function of the adsorption time.



temperature range from 30 to 200 °C may suggest the varied thermal stabilities of these adsorbed species.

Fig. 8 shows the total amount of desorbed NO, NO<sub>2</sub>, O<sub>2</sub>, CO and CO<sub>2</sub> during TPD as a function of adsorption time. The amount of desorbed NO increases linearly with time up to 1 h and then it is almost constant. NO<sub>2</sub> desorption starts at about 5 min and increased slowly before 30 min. After 30 min, the amount of desorbed NO<sub>2</sub> increases rapidly with the adsorption time. The amounts of desorbed O<sub>2</sub>, CO<sub>2</sub>, and CO also increase continuously with the adsorption time, even after the amount of NO reaches maximum. Therefore, desorption of these species is related to both NO and NO<sub>2</sub> desorption. Desorption of NO and NO<sub>2</sub> was also observed during argon purge before TPD test. During argon purge, the amount of NO desorbed after adsorption for 5 min, 30 min, 1 h, 2.5 h, and 24 h is 0.04, 0.12, 0.13, 0.12, and 0.1 mmol/g, respectively; the amount of NO<sub>2</sub> desorbed is 0, 0.005, 0.03, 0.16, and 0.11 mmol/g, respectively.

Based on the data shown in Figs. 2 and 8, the material balance for NO adsorption on SKC-45 carbon was calculated for the adsorption period of 5 min to 24 h. It was found that 90% of the consumed gaseous NO became adsorbed NO species on the carbon surface during the first 5 min of adsorption. After 5 min, some of the gaseous NO was converted into adsorbed NO<sub>2</sub> species. During the first 30 min, 75% of the consumed gaseous NO converted to adsorbed NO, 12% to adsorbed NO<sub>2</sub> and 4% to gaseous NO<sub>2</sub>, respectively. The percentage of gaseous NO<sub>2</sub> increases dramatically after 30 min.

Along with the adsorption of NO, O<sub>2</sub>, and NO<sub>2</sub>, the carbon surface was strongly oxidized during NO + O<sub>2</sub> adsorption. Fig. 9 shows the CO and CO<sub>2</sub> desorption spectra during TPD after exposing the cleaned SKC-45 to various gases. The cleaned carbons were prepared by preheating in argon flow to 950 °C and cooling down under argon flow to room temperature. Then the cleaned carbons were exposed immediately to (a) 500 ppm NO + 10% O<sub>2</sub> for 10–60 min, (b) 500 ppm NO for 30 min, (c) 10% O<sub>2</sub> for 30 min, (d) argon for 30 min or (e) ambient air for 10 days. The gas flow rate for all these tests but ambient air was 0.5 L/min. As shown in Fig. 9, the CO and CO<sub>2</sub> concentrations after exposure to NO or O<sub>2</sub> alone are only slightly higher than the background level (exposure to Ar). It means that the carbon surface was not strongly oxidized by either NO or O<sub>2</sub> alone at ambient temperature. In contrast, after exposure to NO + O<sub>2</sub> for 10 min the carbon surface was oxidized significantly, and the corresponding CO concentration was even higher than that after exposure to air for 10 days. A longer exposure time (1 h) created more surface oxygen containing groups with the intensity of CO and CO<sub>2</sub> signals further higher.

### 3.5. Role of gaseous and surface oxygen in NO adsorption

To further understand the influence of surface oxygen containing groups on NO adsorption, we examined the adsorption behavior of as-received, cleaned and oxidized SKC-45 carbons with and without the presence of 10% O<sub>2</sub> (Figs. 10 and 11). Here, the cleaned carbons were prepared by

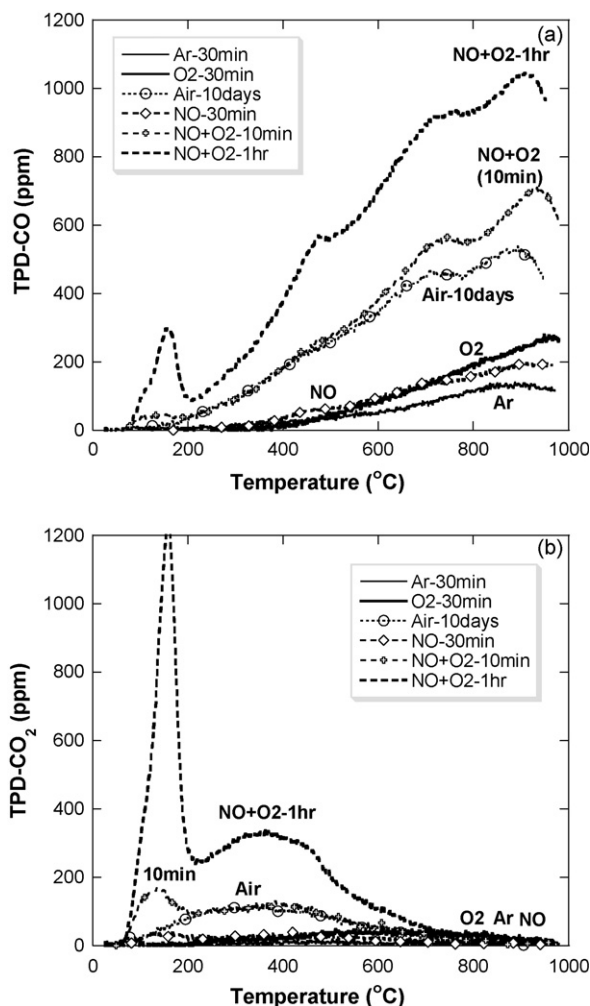


Fig. 9. Desorption spectra of (a) CO and (b) CO<sub>2</sub> from SKC-45 carbon during TPD after exposure of the cleaned carbons to various gases. See text for the details: TPD: 20 °C/min; Ar flow: 0.25 L/min.

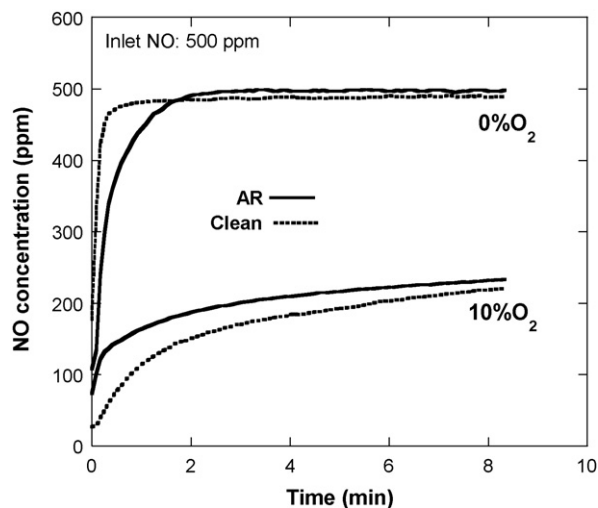


Fig. 10. The effluent NO concentration during NO adsorption on as-received and cleaned SKC-45 carbons at 25 °C in the presence of 0 and 10% O<sub>2</sub>. Flow rate, 0.5 L/min; AC: 0.2 g.

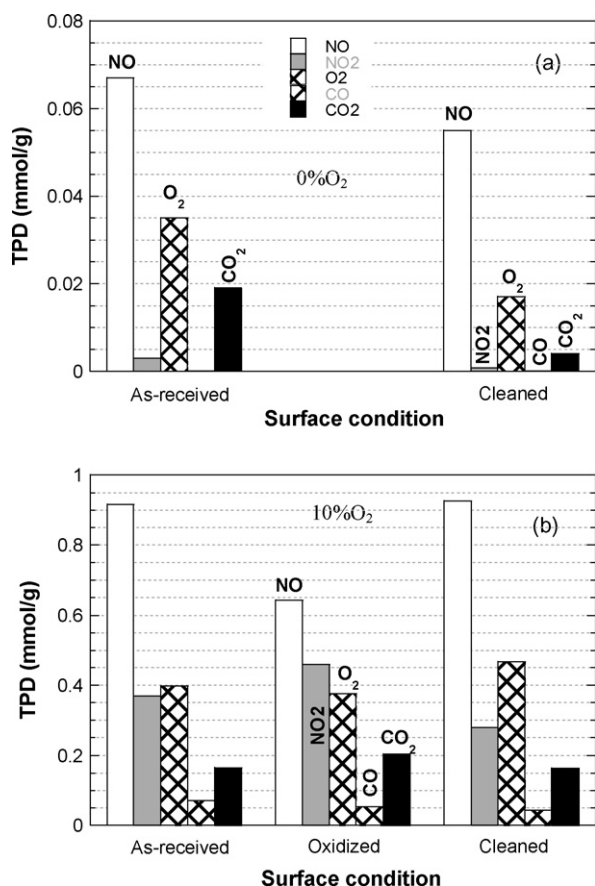


Fig. 11. The amounts of desorbed NO, NO<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, and CO during TPD to 200 °C from (a) as-received and cleaned carbons after 1 h adsorption in 500 ppm NO without O<sub>2</sub>, and from (b) as-received, cleaned and oxidized carbons after 1 h adsorption in the mixture of 500 ppm NO and 10% O<sub>2</sub>; TPD: 10 °C/min; Ar flow: 0.5 L/min.

preheating in argon as mentioned in a previous section. Heating a carbon to 950 °C may slightly anneal the carbon surface. However, the effect on carbon texture is considered to be marginal because the carbon was prepared by activation at 950 °C for over 40 min. The oxidized carbons were prepared by oxidizing the as-received carbon in NO + O<sub>2</sub> gas for 1 h and then running TPD to 200 °C so that the adsorbed NO and NO<sub>2</sub> were desorbed but most of the oxygen containing groups remained on the surface. It is surprising to note that the cleaned carbon had less NO adsorption than the as-received carbon when oxygen was absent (Fig. 10). This is further confirmed by the TPD data shown in Fig. 11a, where the amount of NO desorbed from cleaned carbon is lower than that of the as-received carbon. We believe that this value will be further reduced if the contribution of the oxygen impurities (~400 ppm) in the feed gas to NO adsorption is eliminated.

When O<sub>2</sub> is present, the cleaned SKC-45 initially adsorbs more NO than the as-received one as indicated by its low outlet NO concentration (Fig. 10). However, after 10 min, the adsorption curves are almost identical for both carbons. The amounts of NO desorbed during TPD after 1 h adsorption are almost identical for both carbons (Fig. 11b). The importance of gaseous O<sub>2</sub> in NO adsorption is further evident in Fig. 11. The

amount of desorbed NO is about 15 times higher for both as-received and cleaned carbons when 10% oxygen is present.

## 4. Discussion

### 4.1. NO oxidation on activated carbons

The importance of gaseous oxygen for NO removal on ACs has been reported in many studies [3,4,7–12]. It was postulated that the ACs act as a catalyst to convert NO to NO<sub>2</sub> in the presence of O<sub>2</sub> and then NO<sub>2</sub> adsorbed on the carbon surface [7–9,15]. However, the process of NO oxidation on AC has not been fully understood yet. Ahmed et al. [12] suggested that NO is oxidized by oxygen to NO<sub>2</sub> in the gas phase and then NO<sub>2</sub> is adsorbed on the carbon surface. They pointed out later that the homogeneous oxidation of NO in gas phase is too slow to count for the observed NO oxidation on ACs. The second proposed route was that NO reacts with the surface oxygen atoms which are formed by the reaction between gas phase O<sub>2</sub> and AC [2,4]. But this argument is difficult to reconcile with the observation that pre-adsorption of O<sub>2</sub> on ACs did not increase NO adsorption [8,12]. Actually, oxidation of ACs by gaseous oxygen is a very slow process as shown in Fig. 9.

The experimental results in this study suggest strongly that this catalytic reaction involves the micropores of activated carbons. As shown in Fig. 3, NO to NO<sub>2</sub> conversion reaches the maximum on the AC with an average micropore size close to 7 Å, and this conversion is independent of the surface areas. One interesting fact is that the kinetic diameters of O<sub>2</sub> and NO are 3.46 and 3.17 Å, respectively [1]. Therefore, if O<sub>2</sub> and NO molecules co-adsorb in these narrow micropores of about 7 Å, they will have to contact very closely each other. Since the reaction is first-order with respect to NO and half-order to O<sub>2</sub> (Figs. 5 and 6), we proposed the overall reaction as  $\text{NO} + 1/2(\text{O}_2) \rightarrow \text{NO}_2$  which involves the dissociation of co-adsorbed oxygen with NO in the micropores:  $\text{O}_2 \rightarrow 2[\text{O}]$ . These observed reaction orders seem not support the other possible mechanism proposed for gas phase NO oxidation through dimerization, that is  $2\text{NO} + \text{O}_2 = (\text{NO})_2 + \text{O}_2 = 2\text{NO}_2$ . The calculated low-apparent activation energy of  $-18.5$  kJ/mol indicates that this reaction is probably limited by the co-adsorption of NO and O<sub>2</sub> (physisorption or weakly chemisorption) in the micropores. The negative apparent activation energy, in other words, the decrease of reaction rate with increasing temperature, may be due to the reduced adsorbed NO and/or O<sub>2</sub> concentrations on the carbon surface at increased temperatures. In addition, this energy value is apparently lower than the dissociation energy of O<sub>2</sub> molecule (493.4 kJ/mol) and the dissociation energy of a C–O bond (345 kJ/mol) at 273 K [16]. Therefore, we speculate that the dissociation of adsorbed oxygen involved in this reaction may be catalytically promoted by the presence of NO, the carbon surface and by the overlapping force fields of the opposite walls within the micropores. In other words, the narrow micropores in ACs act as a nano-catalytic reactor for NO oxidation. It has been known that narrow micropores are very important for gas adsorption [17–19]. The ideal ACs for methane storage should have

micropores with size and shape corresponding to two layers of methane molecules ( $\sim 8$  Å) [17]. The optimum pore size favorable for  $\text{SO}_2$  oxidation on ACs is also  $\sim 7$  Å [18].

This likely reaction model is consistent with our experimental observations. Note first that the presence of oxygen also increases significantly the amount of physisorbed NO on SKC carbons (see discussion in Section 4.3). Since co-adsorption of  $\text{O}_2$  and NO in the micropore is the first step of this reaction, temperature increase will decrease the NO conversion due to the reduced NO adsorption on AC. The second step of this reaction involves the dissociation of oxygen, which is in agreement with the observation that NO conversion is proportional to the square root of oxygen concentration (Fig. 5b). Moreover, as being expected, this reaction was observed to be independent of surface area, pre-oxidation and carbon type but dependent on the volume of narrow micropores (Table 1).

The other possible way for  $\text{NO}_2$  formation is through  $4\text{NO} \rightarrow 2(\text{NO})_2 \rightarrow 2\text{NO}_2 + \text{N}_2$ . This reaction, if it occurred, played a negligible role in the studied condition, because: (a) nearly no NO conversion was observed when oxygen is absent (Fig. 10); (b) no noticeable  $\text{N}_2$  formation was detected.

#### 4.2. $\text{NO}_2$ adsorption on activated carbons

Once  $\text{NO}_2$  has formed, it may adsorb on activated carbon, release as gaseous  $\text{NO}_2$ , or react with carbon surface.  $\text{NO}_2$  was considered by many to be the adsorbed species on ACs [7–9,15], because the critical temperature of  $\text{NO}_2$  is much higher than that of NO. Moreover, the breakthrough of  $\text{NO}_2$  was often observed in many studies to be delayed as compared to NO (Fig. 2b). This delayed release of gaseous  $\text{NO}_2$  was thought to be a result of selective adsorption of  $\text{NO}_2$  on the carbon surface [4,8,9]. However, our TPD test suggested that the adsorbed species are mostly NO but not  $\text{NO}_2$  after 5-min adsorption (Fig. 7a). During the initial 5 min, over 90% of the NO consumed was converted into adsorbed NO. We consider the absence of adsorbed  $\text{NO}_2$  during the initial period is due to the instability of  $\text{NO}_2$  on the tested carbons, which have not been extensively oxidized. To be reported elsewhere [20], we found that  $\text{NO}_2$  gas will decompose completely into NO gas, adsorbed NO and oxygen on activated carbons during the first 20 min of test when we passed 500 ppm  $\text{NO}_2$  through the carbon bed at ambient temperature. As the carbon was being slowly oxidized, the outlet  $\text{NO}_2$  concentration gradually increased while the NO concentration decreased. A similar process seems to take place during the early stage of adsorption in NO +  $\text{O}_2$  mixture. Once  $\text{NO}_2$  forms in the micropores, it may migrate to the active carbon sites, oxidizing these sites and leaving the adsorbed NO on the surface. After these sites have been oxidized,  $\text{NO}_2$  becomes stable on the surface either as adsorbed species or is released as gas. Therefore, we believe that the delayed  $\text{NO}_2$  breakthrough is not due to the selective  $\text{NO}_2$  adsorption but mainly due to  $\text{NO}_2$  decomposition.

The proposed  $\text{NO}_2$  decomposition mechanism is supported by experimental results. First, we observed that the carbon surface was rapidly oxidized during the initial 10 min of

adsorption in NO +  $\text{O}_2$  (Fig. 9). The amount of CO desorbed during TPD after 10 min adsorption is 0.77 mmol/g, and it increases by merely 0.51 mmol/g after additional 50-min adsorption. Meanwhile, most of the consumed NO transformed into adsorbed NO during the same period. Second, the delayed times for  $\text{NO}_2$  release on different carbons are apparently related to the extent of surface oxidation. The delayed periods for carbons in Fig. 2b follow the sequence of SKC-AR < SKC-45 < SKC-360, which is the inverse order of the amount of surface oxygen groups on these carbons (Fig. 4).  $\text{NO}_2$  was also observed to release earlier on the oxidized SKC-45 as compared to the as-received one. In addition, both the amounts of adsorbed  $\text{NO}_2$  and  $\text{NO}_2$  gas increased rapidly after 30-min adsorption, which we believe is because the carbon surface has been extensively oxidized. All these observations are in agreement with the proposed mechanism.

A large amount of  $\text{NO}_2$  was also physically adsorbed on ACs and released during argon purge before TPD as shown in Table 3. This is reasonable in considering the relatively high critical temperature of  $\text{NO}_2$ . The amount of physisorbed  $\text{NO}_2$  is two times higher on SKC-90 carbons with an average micropore size around 7 Å as compared to the SKC-360 carbon with a micropore size of 12.2 Å. Therefore, physisorption of  $\text{NO}_2$  is probably a micropore filling process.

#### 4.3. NO adsorption on activated carbons

As shown in Fig. 10, oxygen is apparently essential to NO adsorption on ACs under the studied conditions. The steep NO breakthrough curve on cleaned carbon indicates that there was basically no NO adsorption when oxygen was absent. There was also no NO release during the argon purge after adsorption, e.g., no physisorbed NO. The chemisorbed NO observed during TPD after 1-h adsorption (Fig. 11a) probably in large part resulted from the co-adsorption with impurity oxygen present in the feed gas, because co-desorption of  $\text{O}_2$  was observed. It is thus concluded that NO adsorption on clean ACs is almost negligible when oxygen is not available. A previous FT-IR study also suggested that NO adsorption on a carbon surface is very low at room temperature in the absence of oxygen [21]. The presence of surface oxygen groups on carbon may assist slightly the NO adsorption when oxygen gas is absent (Fig. 10, as-received sample). However, the amount of NO adsorbed is still very low (Fig. 11a).

When oxygen gas is present, both physical and chemical adsorption of NO are significantly enhanced. The amount of physisorbed NO on SKC-45 was 0.12 mmol/g after 2.5-h adsorption (Table 3). The strong dependence of physisorbed

Table 3

Amounts of NO and  $\text{NO}_2$  desorbed during argon purge and during TPD on different carbons after adsorption for 2.5 h in 500 ppm NO and 10%  $\text{O}_2$  (mmol/g)

	SKC-AR	SKC-45	SKC-90	SKC-180	SKC-360
NO (purge)	0.05	0.12	0.14	0.15	0.11
$\text{NO}_2$ (purge)	0.10	0.34	0.33	0.30	0.16
NO (TPD)	0.9	1.02	0.92	0.79	0.79
$\text{NO}_2$ (TPD)	0.45	0.77	0.76	0.94	0.91



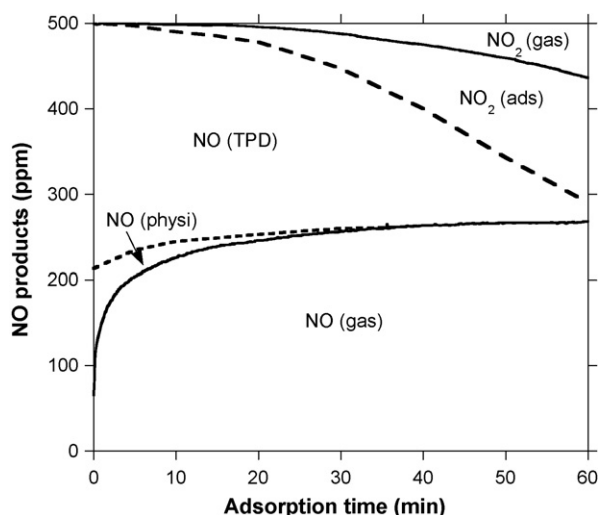


Fig. 12. The estimated NO product distribution at different adsorption times with respect to the inlet NO concentration: AC: SKC-45; 0.2 g; 500 ppm NO + 10% O<sub>2</sub>; flow rate: 0.5 L/min.

NO on oxygen gas leads to the conclusion that NO may co-adsorb physically with O<sub>2</sub> on the carbon surface. During argon purge, these NO molecules desorbed along with desorption of the physisorbed O<sub>2</sub>. A large quantity of NO was also chemisorbed on ACs when oxygen was present (Figs. 8 and 11a). In contrast to physisorption, carbons with small micropores (SKC-AR and SKC-45) have higher amounts of chemisorbed NO than the carbons with relatively larger micropores (SKC-180 and SKC-360) (Table 3). As mentioned in Section 4.2, NO chemisorption on ACs is believed to be a result of NO<sub>2</sub> reduction by carbon along with carbon surface oxidation.

As a summary of the discussion, NO adsorption on activated carbons in the presence of oxygen is a complex and dynamic process involving physical adsorption of NO, co-adsorption of oxygen, reaction of NO and O<sub>2</sub> in narrow micropores, reaction of formed NO<sub>2</sub> with carbon leading to NO chemisorption and oxidation of carbon surface. The product distribution on SKC-45 at different NO adsorption times was estimated from our experimental data and is presented in Fig. 12.

## 5. Conclusions

In this study, a wide range of activated carbons with different porous textures and surface chemistry was examined. We found that activated carbons act as a catalyst for NO oxidation in the presence of oxygen. NO oxidation is related to the presence of

narrow micropores and independent of surface areas, carbon type and surface chemistry. The optimal average micropore size is around 7 Å. The presence of oxygen significantly enhances both physical and chemical adsorption of NO. The adsorbed species on ACs during the initial stage are mainly NO rather than NO<sub>2</sub>. The carbon surface was rapidly oxidized at this stage, and NO<sub>2</sub> adsorption and gas NO<sub>2</sub> release started only after the surface oxidation. Based on these observations, we propose that the narrow micropores serve as a nano-cage for NO/O<sub>2</sub> adsorption and reaction to form NO<sub>2</sub>. The reaction of the formed NO<sub>2</sub> with carbon leads to NO chemisorption and oxidation of carbon surface in the initial period of adsorption.

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